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Measuring the Repassivation Potential of Alloy 22 Using the Potentiodynamic - Galvanostatic - Potentiostatic Method

Kenneth J. Evans, Raul B. Rebak

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Kenneth J. Evans and Raul B. Rebak[1]

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ABSTRACT: Traditionally, the susceptibility of Alloy 22 (N06022) to suffer crevice corrosion has been measured using the Cyclic Potentiodynamic Polarization (CPP) technique (ASTM G 61). When the alloy is not very susceptible to crevice corrosion, the values of repassivation potential obtained using the CPP technique are not highly reproducible. To circumvent the large uncertainty in the values of the repassivation potential by the CPP method, the repassivation potential of Alloy 22 may be measured using a slower method that combines sequentially potentiodynamic, galvanostatic and potentiostatic treatments (this method is called the Tsujikawa-Hisamatsu Electrochemical or THE method). In the THE method the anodic charge is applied to the specimen in a more controlled manner, which avoids driving the alloy to transpassivity and therefore results in more reproducible repassivation potential values. Results using THE method under various testing conditions are presented. A new standard has been prepared for ASTM balloting for the THE method. The round robin matrix results are also discussed.
KEYWORDS: N06022, Crevice Corrosion, Repassivation Potential, Round Robin

Introduction

Alloy 22 contains approximately 56% nickel (Ni), 22% chromium (Cr), 13% molybdenum (Mo), 3% tungsten (W) and 3% iron (Fe) (ASTM B 575) [1]. Because of its high level of Cr, Alloy 22 remains passive in most industrial environments and therefore has an exceptionally low general corrosion rate [2-6]. The combined presence of Cr, Mo and W imparts Alloy 22 with high resistance to localized corrosion such as pitting corrosion and stress corrosion cracking even in hot concentrated chloride (Cl^-) solutions [7-12]. It has been reported that Alloy 22 may suffer localized corrosion such as crevice corrosion when it is anodically polarized in chloride-containing solutions [8-10, 13-15]. It is also known that the presence of nitrate (NO_3^-) in the solution minimizes or eliminates the susceptibility of Alloy 22 to crevice corrosion [8-10, 16-23]. The value of the ratio $R = [NO_3^-]/[Cl^-]$ has a strong effect of the susceptibility of Alloy 22 to crevice corrosion [16-25]. The higher the nitrate to chloride ratio, the stronger is the inhibition by nitrate. It is generally accepted that a minimum ratio R = 0.5 to 1 may be sufficient to inhibit crevice corrosion in Alloy 22. The minimum necessary value of R may depend on other experimental variables such as the total concentration of chloride or the temperature. Other anions in solution were also reported to inhibit crevice corrosion in Alloy 22 [19-20, 26-28].

The susceptibility of Alloy 22 to suffer crevice corrosion is generally measured using the cyclic potentiodynamic polarization (CPP) technique, which is described in the ASTM G 61 standard [29]. This is a fast technique that gives rather accurate and reproducible values of repassivation potential in most cases. In the fringes of susceptibility, when the environment is not highly aggressive, the values of repassivation potential using the CPP technique may not be highly reproducible, especially because the technique is fast and it drives the alloy to the transpassive region of potential without nucleating crevice corrosion. To circumvent this, the

[1] Chemistry, Materials and Life Sciences Directorate, Lawrence Livermore National Laboratory, 7000 East Ave., L-631, Livermore, CA 94551, USA.

repassivation potential of Alloy 22 was measured using a slower method that combines Potentiodynamic-Galvanostatic-Potentiostatic steps (called here the Tsujikawa-Hisamatsu Electrochemical or THE method) [15,30]. The THE method applies the charge to the specimen in a more controlled manner, which gives more reproducible repassivation potential values, especially when the environment is not aggressive.

Due to its excellent resistance to all forms of corrosion, Alloy 22 (N06022) has been selected to fabricate the external shell of the Yucca Mountain high-level nuclear waste containers [18,31]. The environment at the repository site is mostly dry or unsaturated. If water enters in contact with the containers it would be via two main modes: (1) Dripping from the drift crown and walls and (2) Deliquescence of salts or dust collected during the early dry period [32]. The dripping from the drift crown/wall is basically ground water and the main process by which it will enter in contact with the container is generally called seepage. Evaporation may cause these ground waters to concentrate on the engineered barriers. The enrichment of dilute ground waters will follow the chemical divide, that is, the nature and amount of each species that could be present in the final drop of water will depend on the relative amount of species in the originating water [31]. In general, during evaporation of seepage water a high concentration of nitrate will develop, owing to the high solubility of nitrates. This is significant with respect to corrosion performance because the nitrate has inhibiting effects on localized corrosion initiation and propagation, as mentioned above [8-10, 16-23].

The objective of this work was to evaluate a new technique for measuring the crevice repassivation potential, mainly for N06022. This technique is called the Tsujikawa-Hisamatsu Electrochemical (THE) method. The THE method is currently under evaluation by the ASTM to become a new standard under the G-01 “Corrosion of Metals” committee. Repassivation potentials from THE method are compared with repassivation potentials obtained using the traditional method Cyclic Potentiodynamic Polarization (CPP) in the G 61 standard.

Experimental Technique

Alloy 22 specimens were prepared from 1-inch thick plates. The specimens were creviced using a ceramic washer and PTFE tape [15,30]. The specimens could be as-welded (ASW) or non-welded, but they were all multiple creviced. Two types of multi-creviced specimens were used, the prism crevice assembly (PCA) [15] and the lollipop [32]. The lollipop specimen is also called MCA (multiple crevice assembly). The weld in the welded plate was produced with matching filler metal using Gas Tungsten Arc Welding (GTAW). The welded specimens were not all weld metal but contained a weld seam, which varied in width from approximately 8 to 15 mm. The exposed surface area of the specimens varied from approximately 11 cm^2 for the lollipop to 14 cm^2 for the PCA. The specimens had a finished grinding of abrasive paper number 600 approximately 1-h prior to the electrochemical test. The specimens were then degreased in acetone and treated ultrasonically for 5 minutes in de-ionized (DI) water before testing. Each specimen was then sandwiched by a pair of serrated ceramic crevice formers (ASTM G 78) [29], using a Ti Gr 2 bolt and nut to apply the desirable tightness or torque (70 in-lb or 7.9 N-m).

Electrochemical tests were carried out in various electrolyte solutions, from pure chloride (NaCl or $CaCl_2$) solutions to mixtures of chloride plus nitrate to multi-ionic solutions such as basic saturated water (BSW) [32]. The testing temperatures varied from

30°C to 120°C. In most tests nitrogen (N_2) was purged through the solution at a flow rate of 100cc/min for 24 hours while the corrosion potential (E_{corr}) was monitored. Nitrogen bubbling was continued throughout all the electrochemical tests. The electrochemical tests were conducted in a one-liter, three-electrode, borosilicate glass flask (ASTM G 5) [29]. A water-cooled condenser combined with a water trap was used to avoid evaporation of the solution and to prevent the ingress of air (oxygen). All the tests were carried out at ambient pressure. The reference electrode was saturated KCl silver chloride (SSC), which at ambient temperature has a potential of 199 mV more positive than the standard hydrogen electrode (SHE). The reference electrode was connected to the solution through a water-jacketed Luggin probe so that the electrode was maintained at near ambient temperature (see a picture of the set up in Reference 34). The water circulating in the jacket was set at 15°C. The counter electrode was a flag (36 cm²) of platinum foil spot-welded to a platinum wire. All the potentials in this paper are reported in the SSC scale.

Cyclic Potentiodynamic Polarization - CPP: In these tests, the potential scan was started approximately 100 mV below E_{corr} at a set scan rate of 0.167 mV/s. The scan direction was generally reversed when the current density reached 5 mA/cm^2 in the forward scan. In a few tests, the maximum applied potential was 600 mV SSC. Depending on the range of applied potentials, each CPP test could last between 1 h and 3 h. The CPP is a fast and efficient method to determine crevice corrosion resistance of commercial alloys. In the forward scan of the CPP, the potentials for which the current density reaches 20 and 200 µA/cm² are called E20 and E200 (Figure 1). These parameters represent values of breakdown potentials. In the reverse scan of the CPP, the values of potentials for which the current density are 10 and 1 µA/cm² are called ER10 and ER1. The potential at which the reverse scan intersects the forward scan is called repassivation potential cross-over (ERCO). ER10, ER1 and ERCO represent values of repassivation potentials. Figure 1 shows a typical CPP representation with the breakdown and repassivation potentials annotated. The current density in the X-axis was calculated dividing the measured current by the exposed area of the specimen (total area minus the area covered by the crevice formers).

The Tsujikawa-Hisamatsu Electrochemical test - THE: The second test used to assess the susceptibility of Alloy 22 to localized corrosion and passive stability was the Tsujikawa-Hisamatsu Electrochemical test, which currently is under consideration by ASTM to become a standard. This method was named in honor of Shigeo Tsujikawa and Yashihiro Hisamatsu who first reported a multiple combination treatment method (e.g.; potentiodynamic, galvanostatic and potentiostatic) to determine the repassivation potential of stainless steels [33]. For the THE method, the potential scan was started approximately 100 mV below E_{corr} at a set potentiodynamic scan rate of 0.167 mV/s. Once the current density reached a predetermined value (for example 20 µA/cm² or 2 µA/cm²), the controlling mode was switched from potentiodynamic to galvanostatic and the predetermined current density was usually applied for 2 h. The resulting potential at the end of the galvanostatic treatment was recorded. After the galvanostatic step, the treatment was switched to a potentiostatic mode. The potentiostatic steps were applied for 2 h starting at the potential recorded at the end of the galvanostatic treatment minus 10 mV and applying as many steps as necessary until crevice repassivation was achieved. Each subsequent potentiostatic step was 10 mV lower that the previous step. Generally, 10 steps (or a total of 100 mV) were necessary to achieve repassivation of an active crevice-corrosion. Figure 2 shows a typical representation of the THE test. The current density in the left Y-axis was calculated dividing the measured current

by the exposed area of the specimen (total area minus the area covered by the crevice formers). The repassivation potential is determined as the potential for which the current density did not increase as a function of time in the period of treatment of 2 h. Depending on the applied time and number of potentiostatic steps, each THE test could last between 24 h and 30 h. The THE method is a lengthy test, which yields only one parameter, the crevice repassivation potential (ER, CREV). The determination of ER,CREV from the data may be subjective (operator dependent).

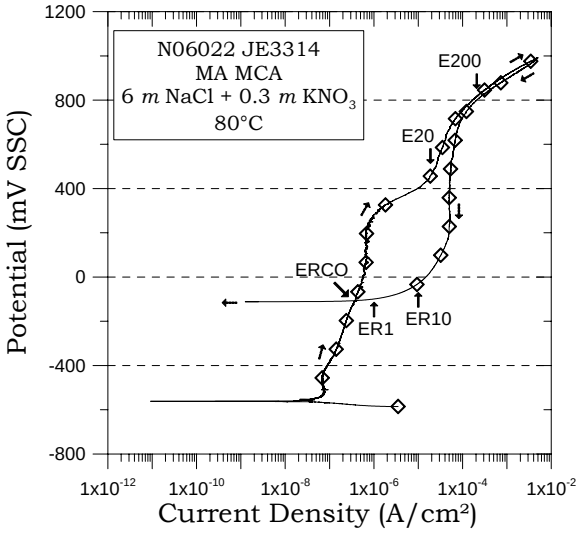

Figure 1. Typical cyclic potentiodynamic polarization ASTM G 61. The breakdown (E20, E200) and repassivation (ER10, ER1, ERCO) potentials are shown.

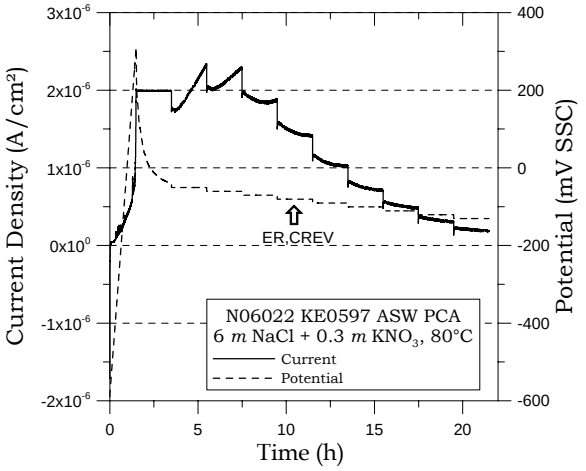

Figure 2. Typical Tsujikawa-Hisamatsu Electrochemical test. The repassivation potential ER,CREV is the constant potential at which the current density did not increase as a function of time.

After the CPP and THE tests, the specimens were examined in an optical stereomicroscope at a magnification of 20 times to establish the mode and location of the attack.

Results in Calcium Chloride Solutions

Figure 3 shows a typical THE test in 5 M $CaCl_2$ solution at 60°C. For Alloy 22 specimen JE1609, the applied galvanostatic current was 20 µA/cm² for 2 hours. During the galvanostatic step the potential decreased as a function of time showing that crevice corrosion had nucleated in the specimen. The decrease in potential during the 2-h galvanostatic treatment was 177 mV (from 245 mV to 68 mV). In the few first potentiostatic steps the current increased as a function of time showing that the crevice corroded area was still active and growing. In the last few potentiostatic steps the increase of current was negligible and in Step 14 the current decreased as a function of time showing that the crevice corroded area was fully passivated. The repassivation potential was -72 mV. At its highest value in Step 2, the current was 261 µA. It could be assumed that most of this measured net anodic current originated from the creviced area. At the time of the repassivation, the current

was 10 µA (this represents approximately 1 µA/cm² taking the entire exposed surface of the specimen).

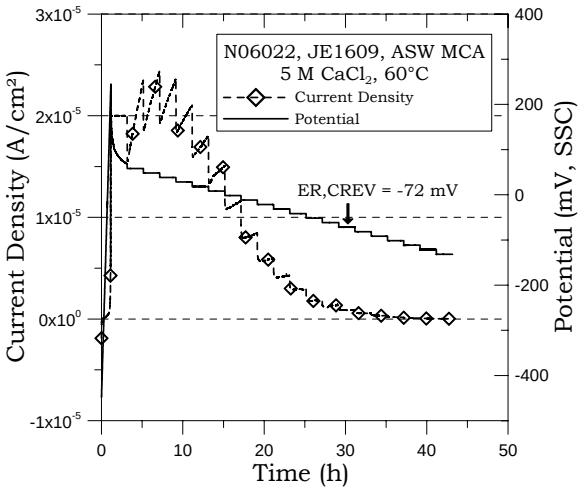

Figure 3. THE test for N06022 in 5 M $CaCl_2$ at 60°C

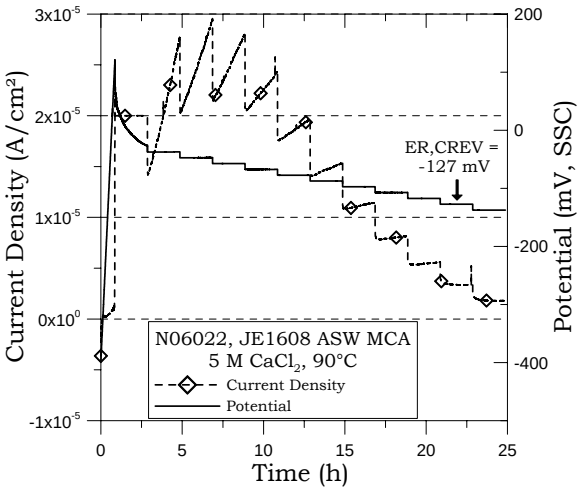

Figure 4. THE test for N06022 in 5 M $CaCl_2$ at 90°C

Figure 4 shows the THE test for Alloy 22 in 5 M $CaCl_2$ at 90°C under the same testing conditions that for 60°C (Figure 3). Again, during the galvanostatic period the potential decreased from 121 mV to -27 mV (a total decrease of 148 mV). It is likely that if the galvanostatic treatment would have continued for longer time, the potential would have continued to decrease until it reached the repassivation potential value. During the potentiostatic steps the current density initially increased showing that the crevice corroding area was growing but in the potentiostatic Step 10, the current decreased showing that the crevice corrosion repassivated. The repassivation potential was -127 mV (Figure 4). The maximum applied current was 316 µA in the potentiostatic Step 2, and when the crevice repassivated the total current was 36 µA.

Figure 5 shows the repassivation potential as a function of the temperature for Alloy 22 in 5 M $CaCl_2$ obtained using the THE method. Some of values of ER,CREV were obtained using 2 µA/cm² in the galvanostatic step and others using 20 µA/cm². For some tests the galvanostatic step could be higher or lower than 2 hours. For one test at 120°C the galvanostatic step was only 10 minutes. See discussion later on the effect of applied charge in the galvanostatic step. Figure 5 shows that the repassivation potential decreased as the temperature increased from approximately 0 mV at 30°C to -130 mV at 90°C (at a rate of 2 mV/K). When the temperature increased from 90°C to 120°C, the repassivation potential only decreased slightly to -135 mV at a rate of 0.2 mV/K (ten times lower than in the lower temperature range). That is, above a certain temperature, there is very little influence of the temperature on the crevice repassivation potential.

Figure 6 shows comparatively the repassivation potential of Alloy 22 using the THE and the CPP methods. The data in Figure 5 is plotted in Figure 6 as full circles and a straight line fit through the full circles is also shown. It is clear that at temperatures lower than approximately 60°C the repassivation potential measured using the CPP method was higher than the repassivation potential using the THE method. This trend was reversed for the

temperature range higher than 60°C. It is also clear from Figure 6 that the measurement of the repassivation potential is highly reproducible at temperatures of 75°C and higher using both methods. However, at temperatures of 60°C and lower, the repassivation potential measured using the CPP method could vary by as much as 800 mV depending on the each test. If during the CPP test the specimen developed earlier crevice corrosion the repassivation potential would be lower (e.g., near 0 mV). However, if the specimen ended the test by undergoing mostly transpassive dissolution rather than nucleating crevice corrosion, the repassivation potential ER1 could be in the order of 800 mV.

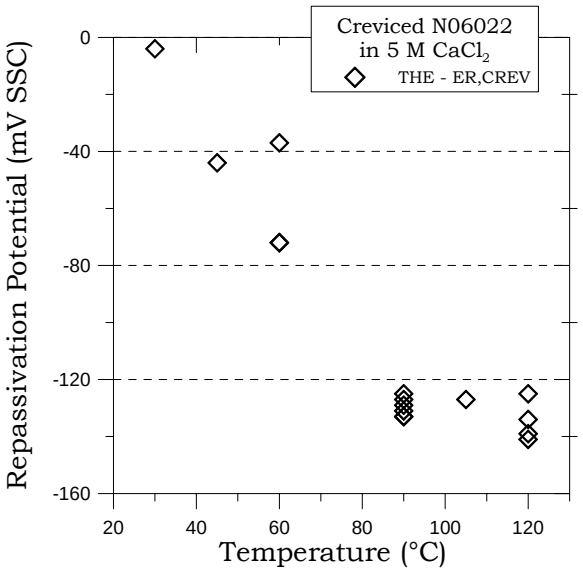

Figure 5. Repassivation potential ER,CREV for Alloy 22 in 5 M $CaCl_2$ using the THE method

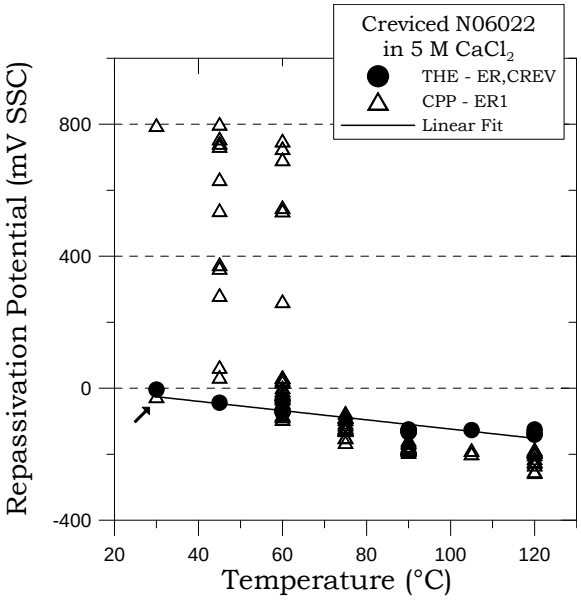

Figure 6. Comparing repassivation potential for Alloy 22 in 5 M $CaCl_2$ using the THE and the CPP methods

Figure 6 shows one CPP point at 30°C marked with an arrow. This ER1 repassivation potential was obtained using a scan rate of 0.0167 mV/sec (ten times lower than the standard G 61 scan rate). It is apparent that a gentler way of applying the charge to the specimen in the CPP test may generate values of repassivation potential comparables to those from the THE test. The conclusion from Figure 6 is that the CPP method could be used to determine the repassivation potential of Alloy 22 if the system is aggressive enough to readily nucleate crevice corrosion (in Figure 6, at a temperature of 75°C or higher). If the system is not highly aggressive (e.g., at temperatures of 60°C and below) the use of the THE method is better suited.

Figures 7 and 8 show the appearance of two lollipop specimens tested in the same electrolyte of 5 M $CaCl_2$ solution at 45°C using two different methods. The images shown (Figures 7 and 8) are from the north-east quadrant of the annular specimen (see Reference 32) and the original magnification is approximately X8. Figure 7 shows the appearance of specimen DEA3229 tested using the CPP method. In this test the potential was driven potentiodynamically to more than 1.2 V before the scan was reversed. The potential vs. current plot did not experience hysteresis in the reverse scan. The repassivation potential ER1

was 365 mV (see also Figure 6). Specimen DEA3229 suffered mainly substantial transpassive dissolution on the boldly exposed surfaces due to the high applied potentials. Very little Type II [21] or dull crevice corrosion was found under a few of the crevice formers.

Figure 8 shows the appearance of specimen JE1633 tested using the THE method. The maximum applied potential in the potentiodynamic step was 159 mV. The applied current in the galvanostatic step was 2 µA/cm². In the galvanostatic step the potential dropped from 159 mV to 46 mV showing that crevice corrosion nucleated and was growing. The crevice corrosion growth was sustained for several potentiostatic steps. The repassivation potential was -44 mV (Figure 6). The specimen suffered only crystallographic Type I [21] crevice corrosion (Figure 8). The boldly exposed surfaces were non-corroded mainly because the maximum applied potential was low, well below transpassivity. All the applied current was used to grow the crevice corroded area.

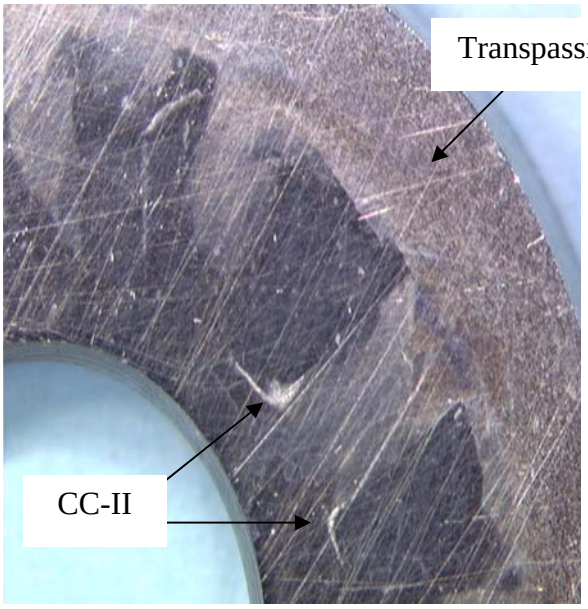

Figure 7. Specimen DEA3229 after the CPP test in 5 M $CaCl_2$ at 45°C. The main mode of attack was transpassivity. Magnification X8. The width of the annular section is 6.5 mm.

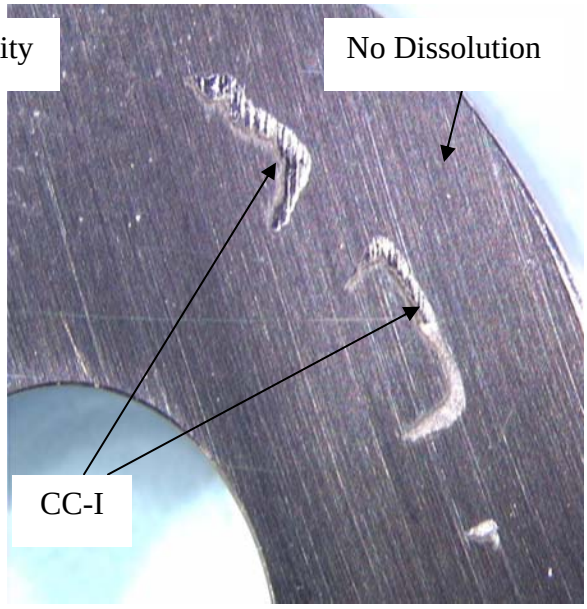

Figure 8. Specimen JE1633 after the THE test in 5 M $CaCl_2$ at 45°C. The main mode of attack was crevice corrosion. Magnification X8. The width of the annular section is 6.5 mm

Results in Sodium Chloride Solutions

Figure 9 shows the ER,CREV repassivation potential for N06022 using the THE method as a function of the chloride concentration at 60°C and 90°C. The applied current density in the galvanostatic step was 2 µA/cm² for 2 hours. At both temperatures, as the logarithm of the chloride concentration increased from 0.0005 M to 1-4 M, the repassivation potential decreased linearly by approximately 300 mV. The repassivation potential at 90°C was approximately 100 mV lower than at 60°C for all the tested chloride concentrations.

Figure 10 shows the effect of the applied current density in the galvanostatic step on the value of the repassivation potential in NaCl solutions. For the higher applied current

density the measured repassivation potential was higher and this effect was more evident at the lower chloride concentration (less aggressive conditions). When a current density of 20 μA/cm² was applied, the specimen was forced to move to the transpassive region of potential well above the value of the repassivation potential. This caused general dissolution of the non-creviced surfaces of the specimen and this effect may have short-circuited crevice initiation under the crevice formers. The effect of applied current in the galvanostatic step was much more important in the solutions prepared with NaCl than in the solutions prepared with $CaCl_2$ (Figure 5). This is in direct relationship with the "shape" of the potential vs. current curve (e.g., CPP) in the solution under consideration. The effect of the amount of current applied was not evident in the $CaCl_2$ solutions, mainly because these solutions were highly concentrated (i.e., highly aggressive).

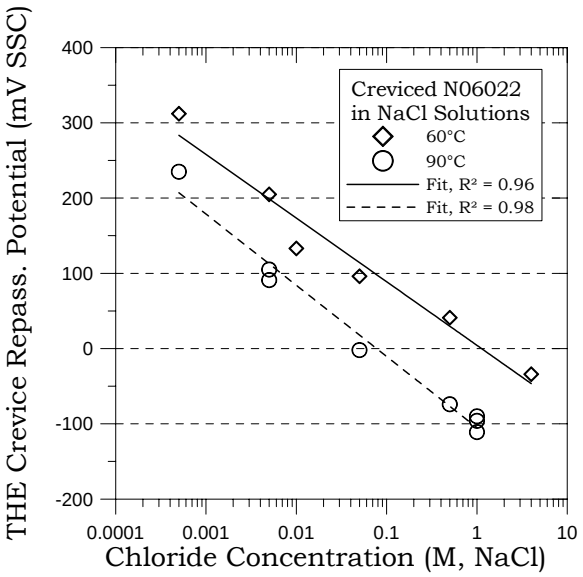

Figure 9. Repassivation potential for N06022 as a function of NaCl concentration

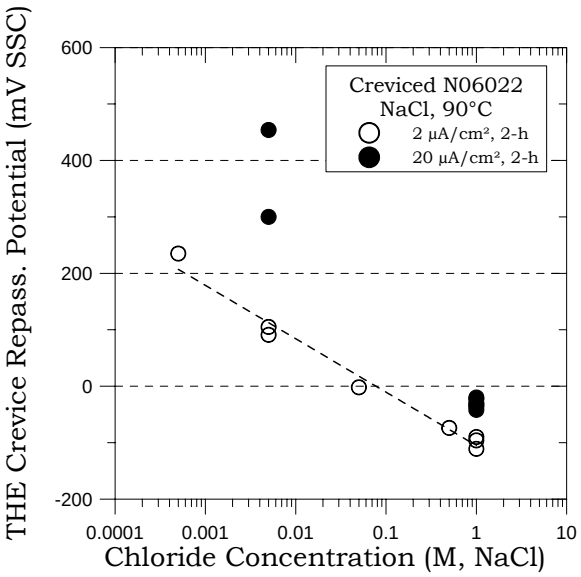

Figure 10. Effect of galvanostatic current on the repassivation potential for N06022 in NaCl solutions.

Results in Chloride plus Nitrate Solutions

The THE method was also applied successfully to determine the resistance to crevice corrosion of Alloy 22 in solutions containing both chloride and nitrate [34]. Chloride is a promoter of crevice corrosion and nitrate is an inhibitor of crevice corrosion. The value of the ratio R = [NO3]/[Cl] is important to determine if crevice corrosion would occur or not in Alloy 22. When this ratio R is higher than approximately 0.5 crevice corrosion will be inhibited. Figure 2 shows the plot of the THE test for specimen KE0597 in 6 m NaCl + 0.3 m KNO_3 solution at 80°C. This solution corresponds to an R value of 0.05. The amount of nitrate in the solution is not sufficient to inhibit crevice corrosion. In Figure 2, during the galvanostatic step of 2 μA/cm² for 2 hours the potential continuously decreased as the time increased, showing that crevice corrosion has been nucleated and that the specimen was becoming more active as time increased. In the first three potentiostatic steps, the current increased showing that at these applied potentials the crevice corrosion area was still active. However, in the third potentiostatic step the current decreased as a function of time showing

that the crevice corrosion area was fully repassivated. The repassivation potential for specimen KE0597 in Figure 2 was –71 mV. The repassivation potential ER1 obtained using the CPP method in 6 m NaCl + 0.3 m KNO_3 at 80°C for specimen JE3314 (Figure 1) was -99 mV. The average value of ER1 for four specimens tested under the same conditions was –80 ± 24 mV [34]. The variation in the standard deviation using the CPP method, for example as the temperature increases and decreases, is discussed further in Reference 34.

Results in Multi-ionic Solutions

The THE method has also been used to determine the repassivation potential of Alloy 22 in multi-ionic solutions that could be representative of concentrated ground waters [32]. Table 1 shows the composition of three multi-ionic solutions used in the laboratory for testing. SCW is simulated concentrated water and it is approximately 1000 times more concentrated than ground water (pH may vary from 8 to 10), SAW is simulated acidified water and it is 1000 times more concentrated than ground water, and it is later acidified to pH 2.8, BSW is basic saturated water and it has a high pH of 13.

Table 1. Chemical composition of the multi-ionic solutions in mg/L

Ion	SCW, pH 8-10	SAW, pH 2.8	BSW, pH 13
K^+	3400	3400	81,480
Na^+	40,900	40,900	231,225
Mg^{2+}	< 1	1000	---
Ca^{2+}	< 1	1000	---
F^-	1400	0	1616
Cl^-	6700	24,250	169,204
NO_3^-	6400	23,000	177,168
SO_4^{2-}	16,700	38,600	16,907
HCO_3^-/CO_3^{2-}	70,000	0	107,171
SiO_2 (aq.)	~ 40	~ 40	9038
$R=[NO_3^-]/[Cl^-]$	0.96	0.95	1.05

Figure 11 shows the THE plot for Alloy 22 for specimen JE1611 in BSW solution at 105°C. Both the potential and the current are plotted as a function of the test time. Figure 11 shows that the potential remained approximately stable during the galvanostatic treatment of 200 μA/cm² for 2-h showing that if crevice corrosion nucleated, it was negligible. During the first two potentiostatic treatments, the current increased as time increased, suggesting that the crevice corrosion was active. However, in the third potentiostatic treatment the current did not increase as a function of time, suggesting that the crevice corroded area ceased to grow. The potential at which the applied current did not increase as a function of time is the ER,CREV or crevice repassivation potential by the THE method. For Figure 11 ER,CREV was +452 mV SSC. Using the CPP method at the standard potential scan rate of 0.167 mV/s, crevice corrosion was not observed in Alloy 22 and the repassivation potential ERCO was reported at +430 mV [32]. Using the CPP method at a scan rate ten times lower than the standard value given in ASTM G 61, crevice corrosion was observed in Alloy 22 and the repassivation potential ERCO was +464 mV [32]. Other results for crevice repassivation potential in SAW, SCE and BSW solutions are listed in Reference 32. Crevice corrosion

could not be initiated in SAW and SCW even using the THE method. Table 1 shows that the ratio R = nitrate over chloride was practically the same for SAW, SCW and BSW. However, the base concentration of chloride in BSW is at least ten times higher in BSW than in the other two electrolytes (SAW and SCW).

The THE method has also been used to determine the repassivation potential of Titanium alloy Grade 7 [35].

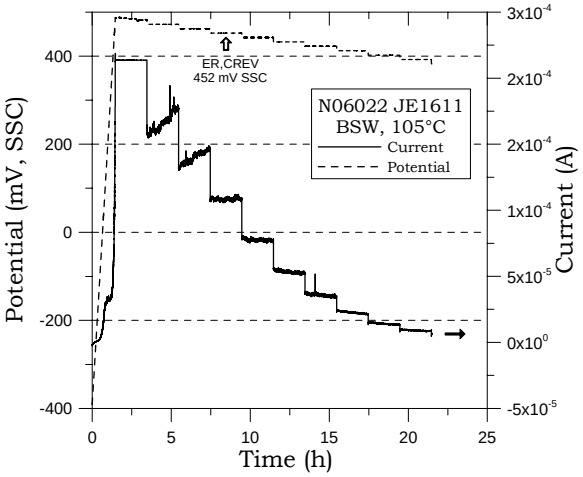

Figure 11. THE test in BSW at 105°C. Crevice corrosion occurred but the repassivation potential was high.

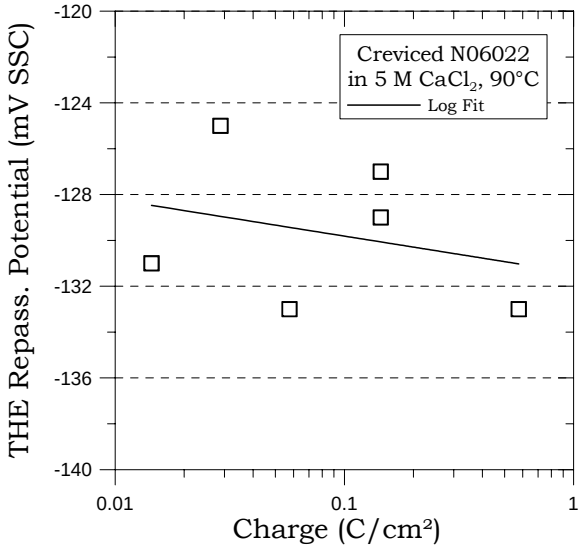

Figure 12. Effect of applied charge on the repassivation potential of Alloy 22 in 5 M $CaCl_2$ at 90°C.

Effect of Applied Current and Charge in the Galvanostatic step

It was mentioned above that the value of the repassivation potential of Alloy 22 in NaCl solutions could depend on the amount of current that is applied in the galvanostatic step. This may not be important for tests of Alloy 22 in 5 M $CaCl_2$ solutions. Six tests were performed in which the applied current density was either 2 or 20 µA/cm². The holding time was between 2 hours and 8 hours (Table 2). Figure 10 and Table 2 show that the applied charge and applied current density have little or no effect on the value of repassivation potential for Alloy 22 in 5 M $CaCl_2$ solution at 90°C within the range of the parameters studied. The effect shown in Figure 12 is insignificant since the repassivation potential decreased only in the order of 2 mV when the charge increased by almost two orders of magnitude. However, these no-effect results are only valid under the reported testing conditions. It may be possible that an effect of applied charge was not detected because the tested solution was rather aggressive and readily nucleated crevice corrosion in Alloy 22.

Effect of Applied Torque and Electrolyte Aeration

In the standard procedure, the crevice formers are tightly attached to the specimens using a high torque of 70 in.lb (7.9 N-m). A high torque was preferred because this will establish a tight crevice and therefore crevice corrosion would be easier to nucleate in Alloy 22. However, it was of interest to determine the effect of the amount of torque on the crevice

repassivation potential of Alloy 22 in 1 M NaCl solution at 90°C. Figure 13 shows that the values of repassivation potential are approximately the same for values of torque of 30 in·lb (3.4 N-m) and higher. However at values of torque lower than 30 in·lb (3.4 N-m) the repassivation potential slightly increased, probably because a larger gap was established between the crevice former and the tested specimen. A similar effect of applied torque on the repassivation potential of Alloy 22 using THE method has been reported also by Jakab and Sridhar [36].

Table 2. Effect of Applied Charge and Current Density in the Galvanostatic step on the Repassivation Potential of Alloy 22 in 5 M $CaCl_2$ at 90°C

Specimen	Current Density ($\mu A/cm^2$)	Time (h)	ER,CREV (mV SSC)
JE1607	20	2	-129
JE1608	20	2	-127
JE1628	2	2	-131
JE1629	2	4	-125
JE1630	2	8	-133
JE1632	20	8	-133

Figure 14 shows the values of the repassivation potential for Alloy 22 in 1 M NaCl solution at 90°C for several different aeration and holding times before the test conditions. Aeration was performed bubbling CO_2-free air through the solution at a rate of 100 cc/min. Figure 14 shows that the repassivation potential was the same for 1 h or 24 hours immersion of the specimen in the deaerated electrolyte before the test is started (Conditions 1 and 2 in Figure 14). Also, the repassivation potential was the same if the specimen was held for 1 week under aerated conditions and later the solution was deaerated for 1 hour (Condition 4). Results from Figure 14 (Condition 3) may seem to suggest that the repassivation potential would be approximately 20 mV lower if the test is performed in aerated electrolytes. However, the value of repassivation potential for Condition 3 was in the same order of the values reported from other laboratories during the round robin test (Figure 15) under deaerated conditions. The result for Condition 3 in Figure 4 was for a single test that may need to be repeated before conclusions are drawn in this matter.

Results from the Round Robin test

In order to prepare a standard for balloting in the ASTM G01 committee, a round robin test was conducted. The tests were for Alloy 22 in 1 M NaCl solution at 90°C using the THE method. The Alloy 22 specimens were non-welded prism crevice assemblies (PCA) creviced with ceramic washers coated with PTFE tape. The applied torque was 70 in.lb. Testing was specified to follow three main steps; (1) A potentiodynamic step at 0.167 mV/s scan rate, (2) a galvanostatic step at 2 $\mu A/cm^2$ for 2 hours and (3) as many as necessary potentiostatic steps to repassivate the specimen. Five specimens and testing hardware were sent to ten different laboratories which initially agreed to conduct these tests. Five other laboratories initially declined to conduct the tests. Of the 10 laboratories that agreed to carry the tests, 9 were in the United States and 1 in Argentina. These laboratories were in

universities, in the private sector and in government institutions. Only 5 laboratories returned the data (Table 3).

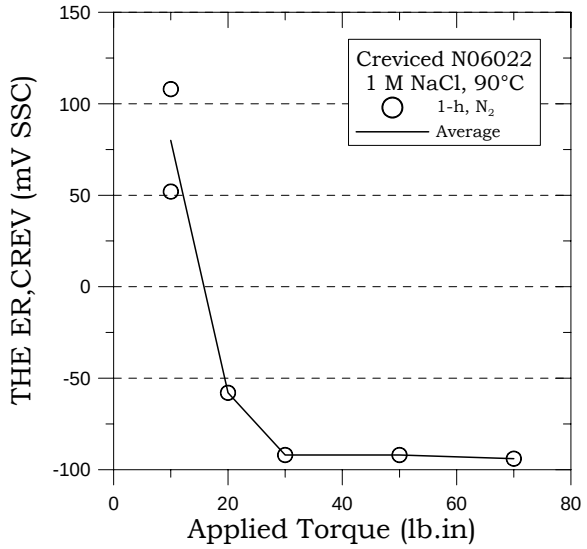

Figure 13. Effect of applied torque on the repassivation potential value of Alloy 22 in 1 M NaCl solution at 90°C

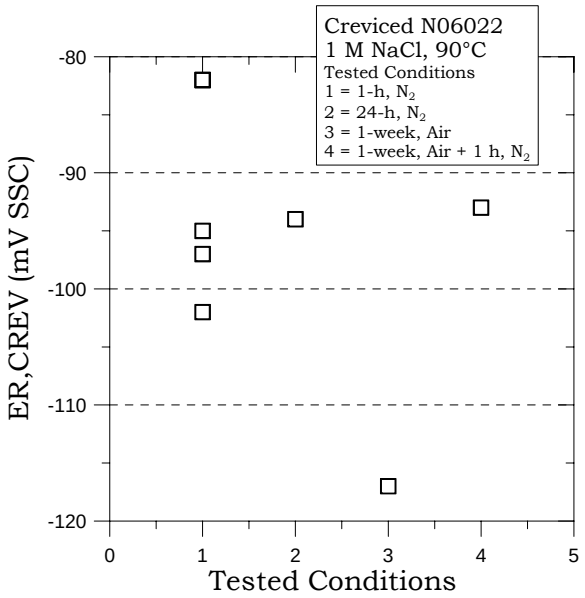

Figure 14. Effect of aeration or deaeration on the repassivation potential value of Alloy 22 in 1 M NaCl solution at 90°C

The results reported by the laboratories were in excellent agreement with each other (Table 3 and Figure 15). The average repassivation potential from all the 5 laboratories was -107 mV and the standard deviation was 10 mV. The lowest value of repassivation potential was for Laboratory 6 and the highest for Laboratory 13. The data from Laboratory 15 showed the highest standard deviation (14 mV) and the data from Laboratory 1 had the lowest standard deviation (5 mV). Two of the participating laboratories (3 and 6) prepared comprehensive reports on the data and the other three returned tabulated data and images of the corroded specimens.

Figure 16 shows the average repassivation potential for Alloy 22 in 1 M NaCl at 90°C using the THE and the CPP methods. For the THE method the repassivation potential was -107±10 mV SSC and for the CPP method the repassivation potential were -69 ± 40 mV SSC (ERCO) and -92±25 mV SSC (ER1). The CPP cross over repassivation potential (ERCO) was higher and had a higher standard deviation than the CPP repassivation potential ER1. The reason for it is because of the shape of the forward CPP curve in this solution. For near neutral NaCl solutions the forward curve is slanted and the cross-over repassivation potential values tend to be higher. Figure 16 also shows that the ER1 CPP repassivation potential was practically the same as the repassivation potential using the THE method, even though the standard deviation for the CPP ER1 was twice as much as for the THE method. In the case of the 1 M NaCl solution at 90°C, the repassivation potentials using both methods (CPP and THE) were close but when the system is not aggressive (see Figure 6) the values of repassivation potentials for both methods could be different by several hundredths of mille volts.

Table 3. Round Robin Test Results

	Lab. 1	Lab. 6	Lab. 13	Lab. 15	Lab. 3	All Labs
Individual Repassivation Potential Values (mV, SSC)	-111	-114	-82	-102	-106	
	-106	-135	-82	-125	-91	
	-116	-110	-97	-100	-110	
	-112	-112	-94			
	-119		-102			
			-95			
Average	-113	-118	-92	-109	-102	-107
Standard Deviation	5	12	8	14	10	10

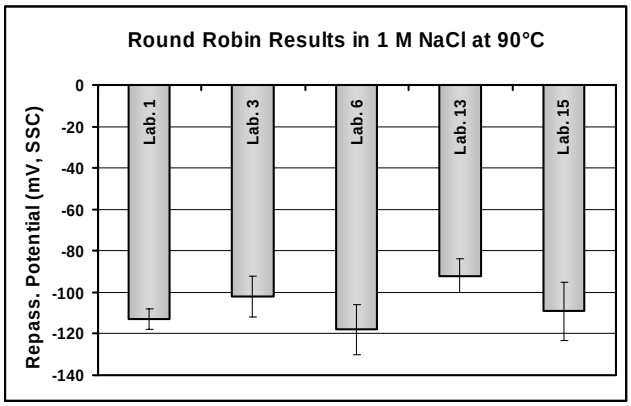

Figure 15. Results from the THE Round Robin test for Alloy 22. Excellent agreement among the five laboratories.

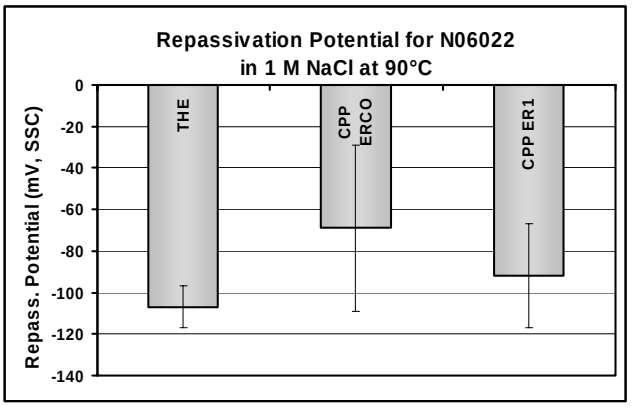

Figure 16. Comparative results of repassivation potentials for the THE and CPP methods.

Summary and Conclusions

The THE method may need to be standardized as a technique to determine the repassivation potential of Alloy 22 and other corrosion resistant alloys.

- The THE method is intended to be used as a complement for the CPP technique given in ASTM G 61.
- Whenever the system is aggressive (e.g., high chloride or high temperature) both the THE and the CPP methods yield similar crevice repassivation potential values.
- In regions of low susceptibility (e.g., low chloride concentration or low temperature) the THE method yields more reproducible values of repassivation potential.
- The THE technique may not used with fixed parameters for all the testing conditions. The parameters (especially the applied current density in the galvanostatic step) may need to be slightly adjusted depending on the type of alloy or testing environments.
- A successful round robin test was carried out and five laboratories reported similar values of repassivation potentials.

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References

1 ASTM International, Standard B575, Vol. 02.04 (ASTM, 2002: West Conshohocken, PA).
2 Haynes International, "Hastelloy C-22 Alloy", Brochure H-2019E (Haynes International, 1997: Kokomo, IN).
3 R. B. Rebak in Corrosion and Environmental Degradation, Volume II, p. 69, Wiley-VCH, Weinheim, Germany (2000).
4 R. B. Rebak and P. Crook, "Nickel Alloys for Corrosive Environments," Advanced Mater. & Proc., 157, 37, 2000.
5 R. B. Rebak and P. Crook, "Influence of the Environment on the General Corrosion Rate of Alloy 22," PVP-Vol. 483 pp. 131-136 (ASME, 2004: New York, NY).
6 R. B. Rebak and Joe H. Payer, "Passive Corrosion Behavior of Alloy 22," ANS Conf. International High Level Radioactive Waste Management, Las Vegas 30Apr-04May 2006.
7 R. B. Rebak and P. Crook, "Improved Pitting and Crevice Corrosion Resistance of Nickel and Cobalt Based Alloys," ECPV 98-17, pp. 289-302 (The Electrochemical Society, 1999: Pennington York, NJ).
8 B. A. Kehler, G. O. Ilevbare and J. R. Scully, Corrosion, 1042 (2001).
9 K. J. Evans and R. B. Rebak in Corrosion Science – A Retrospective and Current Status in Honor of Robert P. Frankenthal, PV 2002-13, p. 344-354 (The Electrochemical Society, 2002: Pennington, NJ).
10 K. J. Evans, S. D. Day, G. O. Ilevbare, M. T. Whalen, K. J. King, G. A. Hust, L. L. Wong, J. C. Estill and R. B. Rebak, PVP-Vol. 467, Transportation, Storage and Disposal of Radioactive Materials – 2003, p. 55 (ASME, 2003: New York, NY).
11 Y-M. Pan, D. S. Dunn and G. A. Cragnolino in Environmentally Assisted Cracking: Predictive Methods for Risk Assessment and Evaluation of Materials, Equipment and Structures, STP 1401, pp. 273-288 (West Conshohocken, PA: ASTM 2000).
12 R. B. Rebak in Environmentally Assisted Cracking: Predictive Methods for Risk Assessment and Evaluation of Materials, Equipment and Structures, STP 1401, pp. 289-300 (West Conshohocken, PA: ASTM 2000).
13 C. S. Brossia, L. Browning, D. S. Dunn, O. C. Moghissi, O. Pensado and L. Yang, "Effect of Environment on the Corrosion of Waste Package and Drip Shield Materials," Publication of the Center for Nuclear Waste Regulatory Analyses (CNWRA 2001-03), September 2001.
14 D. S. Dunn, L. Yang, Y.-M. Pan and G. A. Cragnolino, "Localized Corrosion Susceptibility of Alloy 22," Paper 03697 (NACE International, 2003: Houston, TX).
15 K. J. Evans, A. Yilmaz, S. D. Day, L. L. Wong, J. C. Estill and R. B. Rebak, "Comparison of Electrochemical Methods to Determine Crevice Corrosion Repassivation Potential of Alloy 22 in Chloride Solutions," JOM, p. 56, January 2005.
16 G. A. Cragnolino, D. S. Dunn and Y.-M. Pan, "Localized Corrosion Susceptibility of Alloy 22 as a Waste Package Container Material," Scientific Basis for Nuclear Waste Management XXV, Vol. 713 (Materials Research Society 2002: Warrendale, PA).
17 D. S. Dunn and C. S. Brossia, "Assessment of Passive and Localized Corrosion Processes for Alloy 22 as a High-Level Nuclear Waste Container Material," Paper 02548 (NACE International, 2002: Houston, TX).
18 J. H. Lee, T. Summers and R. B. Rebak, "A Performance Assessment Model for Localized Corrosion Susceptibility of Alloy 22 in Chloride Containing Brines for High Level Nuclear Waste Disposal Container," Paper 04692 (NACE International, 2004: Houston, TX).
19 D. S. Dunn, L. Yang, C. Wu and G. A. Cragnolino, Material Research Society Symposium, Spring 2004, San Francisco, Proc. Vol. 824 (MRS, 2004: Warrendale, PA).
20 D. S. Dunn, Y.-M. Pan, L. Yang and G. A Cragnolino and X. He, "Localized Corrosion Resistance and Mechanical Properties of Alloy 22 Waste Package Outer Containers" JOM, January 2005, pp 49-55.

21 R. B. Rebak, “Factors Affecting the Crevice Corrosion Susceptibility of Alloy 22,” Paper 05610, Corrosion/2005 (NACE International, 2005: Houston, TX).
22 D. S. Dunn, Y.-M. Pan, L. Yang and G. A Cragnolino, Corrosion, 61, 11, 1078, 2005.
23 G. O. Ilevbare, K. J. King, S. R. Gordon, H. A. Elayat, G. E. Gdowski and T. S. E. Gdowski, Journal of The Electrochemical Society, 152, 12, B547-B554, 2005.
24 M. A. Rodriguez, M. L. Stuart and R. B. Rebak, “Long-Term Electrochemical Behavior of Creviced and Non-Creviced Alloy 22 in CaCl2 + Ca(NO3)2 Brines at 155°C,” Paper 07577, Corrosion/2007, March 2007, Nashville TN (NACE International, 2007: Houston TX).
25 D. S. Dunn, Y.-M. Pan, L. Yang and G. A. Cragnolino, Corrosion, 62, 3 (2006).
26 G. O. Ilevbare, Corrosion, 62, 340 (2006).
27 R. M. Carranza, M. A. Rodriguez and R. B. Rebak, “Inhibition of Chloride Induced Crevice Corrosion in Alloy 22 by Fluoride Ions,” Paper 06622, Corrosion/2006, NACE International, March 12-16, 2006, San Diego, CA (NACE International, Houston, TX).
28 R. B. Rebak, “Mechanisms of Inhibition of Crevice Corrosion in Alloy 22,” in proceedings of Scientific Basis for Nuclear Waste Management XXX, (MRS, 2006: Warrendale, PA).
29 ASTM International, Volume 03.02 “Wear and Erosion; Metal Corrosion” (ASTM International, 2003: West Conshohocken, PA).
30 K. J. Evans, L. L. Wong and R. B. Rebak “Determination of the Crevice Repassivation Potential of Alloy 22 by a Potentiodynamic-Galvanostatic-Potentiostatic Method,” PVP-ASME Vol. 483, pp. 137-149 (American Society of Mechanical Engineers, 2004: New York, NY).
31 G. M. Gordon, Corrosion, 58, 811 (2002).
32 R. B. Rebak, K. J. Evans and G. O. Ilevbare, Corrosion/2007, Paper 07584 (NACE International, 2007: Houston, TX).
33 S. Tsujikawa and Y. Hisamatsu, Corr. Eng. Japan, 29, 37 (1980).
34 K. J. Evans and R. B. Rebak, “Repassivation Potential of Alloy 22 in Chloride plus Nitrate Solutions Using the Potentiodynamic-Galvanostatic-Potentiostatic Method,” in proceedings of the Materials Research Society Fall Meeting, 27 November to 01 December 2006, Boston Massachusetts, paper NN3.13, Volume 985.
35 K. J. Evans and R. B. Rebak, “Anodic Polarization Behavior of Titanium Grade 7 in Dust Deliquescence Salt Environments,” Paper PVP200726161, ASME-PVP Conference, San Antonio, TX, 22-27 July 2007.
36 M. A. Jakab and N. Sridhar “Effect of Torque and Charge Density on the Crevice Repassivation Potential of Ni-Cr-Mo-W Alloys Measured by Modified THE Method,” Research in Progress Symposium, Passivity and Localized Corrosion, Corrosion/2007, NACE International, 11-15 March, 2007, Nashville, TN.